Use of extension variance in monitoring of fluoride in bottled water

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ABSTRACT

Temporal variograms allowed the analyzing of the temporal variance of eight sources of mineral waters during the four climatic seasons. The water sources are located in the state of São Paulo, Brazil. The extension variance compares the temporal variance obtained in the collection interval t with the temporal variance obtained in the collection interval T (where T is twice as large as t). Based on the calculation of the extension variance, relative sampling errors for the confidence intervals (CI) equal to 68% and 99% were obtained. For the sampled sources, the greater the sampling interval, the greater the values obtained for the extension variance and for the relative sampling error. The greater the confidence interval analyzed, the greater the relative sampling error to be obtained. The results showed a very high global sampling error for collection intervals greater than 32 days (relative error greater than 10%) when the confidence interval was CI = 68%. When the confidence interval was 99.9%, for collection intervals greater than two days, relative sampling errors greater than 10% have already been obtained. It was concluded that for the fluoride parameter the sampling time should not be longer than two days.

Key words | bottled water, extension variance, fluoride, groundwater, relative error, variograms

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HIGHLIGHTS

- We analyzed the fluoride parameter for eight sources of Brazilian mineral waters during different climatic seasons.
- To analyze the time variance of fluoride, temporal variograms were built for the data sets obtained in chemical analyses.
- The average variograms for time intervals that started at $t = 1$ day and ended at $t = 2{,}048$ days were calculated. The extension variance was obtained for $t = 1$ day to $t = 1{,}024$ days.

INTRODUCTION

The sampling of fluoride in bottled mineral water is a complex process because it involves several steps such as: compliance with current legislation, compliance with international sampling protocols that are described in manuals and lastly, sampling must take into account cyclicality for the measured values and the seasonality occurring in the hydrogeochemical parameters, when defining the number of minimum samples to be collected and what is the most appropriate sampling interval for the samples coming from the wells and the final bottled product.

Legislation is not a cause for concern in this work because each country has its own regulation on the accepted levels of fluoride in mineral water (Senior & Dege 2005). In addition, most countries follow the standards established by WHO (2017) on water drinking standards. Other countries follows the water potability standards established by ISO (2009). Both ISO (2009)

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and WHO (2017) legislation are complete and well documented regarding the sampling scope of all water quality parameters.

The mineral water sampling protocols are also not a cause for concern and questioning for the present work, since all the sampling methodologies and measurement of water quality parameters are well explained and documented in the handbook of *Standard Methods for Examination of Water and Wastewater* from the American Public Health Association (APHA 2017) and also in the Environmental Protection Agency manuals (USEPA 1986).

The scope of this work is to determine the number of minimum samples for fluoride that take into account not only the variability of this parameter and its heterogeneity, but also consider the seasonality of fluoride, its cyclic behavior and especially sampling errors due to the fact that fluoride is a trace element in mineral water (Pitard 1993).

It would be much easier to choose a minimum number of samples greater than or equal to 30 and consider that the continuous random variable, which is fluoride, follows a normal Gaussian distribution (Montgomery & Runger 2003). But the fluoride variable, besides being a random variable, is also a regionalized variable. Thus, fluoride as a regionalized variable has two contradictory aspects to know about: the random aspect that considers local irregularities, and the structured aspect that reflects its value trends at large scales (Armstrong 1998).

Since fluoride is a regionalized variable, the present work proposes to first determine the best sampling interval for fluoride from different sources based on temporal variograms for fluoride and on calculating the extension variance based on the obtained variograms.

The extension variance will be obtained for several time intervals, and the relative standard sampling deviation (Pearson's coefficient) will be calculated and based on this calculation the sampling error will be obtained (Pitard 1993). It will conclude if it is better to collect samples from a source every one day, two days, four days, eight days and so on, based on the sampling errors obtained by calculating the variance.

The attempt was made to take samples from sources that belong to the same aquifer to find out if there is any correspondence between the results obtained. And the attempt was made to vary the way of sampling the sources that belong to the same aquifer, to see if there is any influence on the results obtained.

Many past studies have used spatio-temporal variograms to analyze water quality variables. To exemplify, there have been analyses for fluoride in the wet season and in the dry season that occur in Iran. Spatio-temporal variations were established for these seasons. The space-time variations in the two seasons were compared with the standards established in the current legislation for fluoride (Sheikhy Narany *et al.* 2014).

In another study, fluoride was monitored during three important periods in India: pre-monsoon; mid-monsoon and post-monsoon. Spatio-temporal distribution maps of fluoride concentration were made for each of the three periods. The three periods of the monsoon phenomenon were compared in order to be able to ascertain the greatest contamination of water by fluoride that could occur (Beg 2009).

Most of the previous studies on fluoride in groundwater have focused on the use of spatio-temporal variograms to separately analyze the variation of fluoride within each weather season. In these works, the data were grouped by weather season and studied using spatio-temporal variograms and other geostatistical techniques.

But in the present work, the chemical analysis data for fluoride are collected in different weather seasons so that they can be analyzed together by calculating the extension variance. This variance was obtained through temporal variograms for each source of mineral water studied.

The comparison will not be made among the variances of fluoride obtained in the different weather seasons that this anion was sampled. The objective of this paper is to analyze the total variance of fluoride throughout the sampling period. Using the extension variance, it will be possible to visualize what is the percentage of the total variance that can be attributed to each weather season. It is possible to see in which weather season the largest part of the total variance of the data is reached, when using the concept of extension variance.

MATERIALS AND METHODS

We sampled eight natural water sources in Brazil through wells to which we had access and verified if the number of samples and the interval of sampling were adequate for the monitoring purposes of fluoride and classification of

the mineral waters. The statistical tools applied to these analyses are explained after the description of laboratory essays for fluoride and pH determination.

The main characteristics of these sources and the aquifer in which they are located are disposed in Table 1.

The Sonja and Santo Antonio sources have been sampled for more than a year. The volume of the samples varied from small bottles with 300 ml or 500 ml to gallons of 1, 5,10 and 20 litres. We collected one sample for each climatic season at minimum, except at Veronica well, which was sampled only during autumn and winter, and at Juliana well, which was sampled only during winter. In addition, we collected a minor number of samples during spring and summer from the Santa Lucia well. In despite of a great variation regarding the support of the samples (original volume of each sample, total number of samples collected or number of samples collected by season), we had expected to observe a low variability regarding the fluoride parameter inclusive for sources of different aquifers.

The fluoride analyses were made according to the method USEPA 300.1 (USEPA 1986), an international standard, which recommends a colorimetric technique named 'SPADNS' due to the use of 4,5-dihydroxy-3-parasulfophenylazo-2,7-naphthalene-di-sulfonic acid (Dovidauskas *et al.* 2015). In the presence of this complex, the solution/sample loses color proportionally to the fluoride content. The amount of indicator (zirconium solution/SPADNS) put into the sample is a critical parameter, as small variations in the volume of the sample can reflect different colors at the end. This essay consists in: (1) pipetting 10 ml of sample into the cuvette; (2) adding 2 ml of FL-SP Unique; (3) closing and shaking it before leading the cuvette into the calorimeter. All essays were made at laboratory temperatures between 19° and 21 °C.

It is impossible to know the initial concentration of fluoride. We can only determine the final concentration of fluoride through the SPADNS method. We just know the content of fluoride that is described on the label of the bottles of mineral water. The value obtained for fluoride in the SPADNS method is always different from the value of fluoride described on the label of the mineral water.

Regarding pH measurements, these were made according to the procedure SM 23 4500-H^+B described in the book of *Standard Methods for the Examination of Water and Wastewater* (APHA 2017).

After all data was obtained in the laboratory, the first step consisted in analyzing a statistical summary (mean, median, deviation, variation coefficient, quartiles, etc.) for each mineral water well. It was checked whether the number of samples was enough to assume that the data followed a normal distribution. Then, the following equation (Montgomery & Runger 2003) was applied to determine an error as a function of the number of samples for 90%, 95% and 99% confidence levels:

$$n = \left(\frac{z_c \sigma}{E}\right)^2 \quad (1)$$

where:

n = minimum number of samples
z_c = critical value tabled according to the required confidence level
E = expected error margin
σ = standard deviation.

The temporal variance was calculated based on the equation (Armstrong 1998) below, and we plotted the omnidirectional variograms according to the data set obtained for each water well:

$$\gamma(t) = 0.5[\mathrm{Var}(Z(t+\Delta t)) + \mathrm{Var}(Z(t))] = \sigma^2 \quad (2)$$

Table 1 | Water sources description

Source	Local	Classification	Aquifer
(1) Santo Antonio	São Paulo	Fluoridated	Precambrian Aquifer
(2) Sonja	São Paulo	Fluoridated and lithiated	Precambrian Aquifer
(3) Santa Lúcia	São Paulo	Fluoridated	Precambrian Aquifer
(4) Primavera	São Paulo	Fluoridated	Precambrian Aquifer
(5) Juliana	Serra Negra	Fluoridated	Tubarão
(6) Veronica	Negra	Fluoridated	Tubarão
(7) Água Santa	Campos de Jordão	Fluoridated	Tubarão
(8) Ycuara	Mogi das Cruzes	Fluoridated	São Paulo

where Δt is a sampling time interval (days); σ^2 is the variance of fluoride content along different time intervals; $Z(t)$ is the fluoride content in time; and $Z(t + \Delta t)$ is the fluoride content at t plus Δt.

We tested tree models to fit a function which could better represent the variance of these experimental data through time (Armstrong 1998): Spherical (Equation (3)), Exponential (Equation (4)) and Gaussian (Equation (5)). All this procedure can be better understood reading (Isaaks & Srivastava (1989), Goovaerts (1997), Deutsch & Journel (1998) and Remy *et al.* (2009). Variables of our concern were: time interval of sampling in days (t); the range of each variogram for each water well (a), the nugget effect (C_0) and the sill or contribution (C_1).

$$\begin{cases} \gamma(t) = C_0 + C_1\left[1.5\left(\frac{t}{a}\right) - 0.5\left(\frac{t}{a}\right)^3\right], & t < a \\ \gamma(t) = C_0 + C_1, & t \geq a \end{cases} \quad (3)$$

$$\gamma(t) = C_0 + C_1\left[1 - e^{-\left(\frac{t}{a}\right)}\right], \quad t \neq 0 \quad (4)$$

$$\gamma(t) = C_0 + C_1\left[1 - e^{-\left(\frac{t}{a}\right)^2}\right], \quad t \neq 0 \quad (5)$$

The variograms were calculated and fitted by SGeMS (academic version software) and GSLib (Geostatistics Software Library developed by Stanford University – Deutsch & Journel 1998) for extension variance calculation. The calculus of the extension variance is an estimation of the precision error committed when we take samples in longer time intervals regarding the minimum interval in which is possible to collect samples. In this study, the minimum interval was one day ($t_{\min}$), and we would like to measure the error if we had collected every two days (t), every four days ($T = 2t$) and so on.

The following equation was used to determine the extension variance (Wackernagel 1995):

$$\sigma^2_{\text{ext}}(t_{\min}/T = 2\bar{\gamma}(t_{\min}/t) - \bar{\gamma}(t_{\min}/T) \quad (6)$$

where $\sigma^2_{\text{ext}}(t_{\min}/T)$ is the extension variance or committed error due to 'extending' the variance of a population made by samples collected every day for a population collected every four days; $\bar{\gamma}(t_{\min}/t)$ is the variance of the dispersion of a population regarding a short time interval t (two days, for example); and $\bar{\gamma}(t_{min}/T)$ is the variance regarding a longer time interval, which is double the interval t.

As there are several variograms within a time interval t or T, we must calculate a mean variogram $\bar{\gamma}$ for each new time interval. This was made by the 'gammabar' algorithm of the GSLib: the input parameters (a, C_0, C_1) came from the fit of the original variogram. The original variogram was calculated based on the population collected at the minimum time interval which was possible (one day, in this case).

The original variograms were calculated starting from t equal to one day and finishing at 2,048 days, consisting in pairs grouping or σ^2 for Δt equal to 2 up to 1,024.

After all that, we calculated an imprecision due to the extension error for three confidence interval levels (CI): 68%, 95% and 99.9%. According to authors Montgomery & Runger (2003):

$$\sigma^2_{\text{Rel}} = \frac{\sigma^2_{\text{Abs}}}{X^2} \quad (7)$$

where σ^2_{Rel} is the relative variance; X^2 is the quadratic mean of the original data; and σ^2_{Abs} is the absolute variance.

$$\sigma_{\text{Rel}} = \sqrt{\sigma^2_{\text{Rel}}} \quad (8)$$

Errors for CI equal to 68%, 95% and 99% respectively are calculated as: $\pm\, \sigma_{\text{Rel}} \,.\, \bar{X}$, $\pm\, 2\sigma_{\text{Rel}} \,.\, \bar{X}$ and $\pm\, 3\sigma_{\text{Rel}} \,.\, \bar{X}$.

Adding the value of the relative deviation plus the mean of fluoride, the maximum value for fluoride was obtained. Subtracting the relative deviation from the mean of fluoride, the minimum value for fluoride was obtained.

Water is classified as fluoridated when it has at minimum 0.02 milligrams per litre of fluoride in its composition (Senior & Dege 2005). If the sampling presents a high imprecision (high nugget effect and extension variance), it cannot be possible to classify the natural water source with reasonable reliability.

Neither replicates nor duplicates were used for the following wells: Ycuara, Primavera, Água Santa and Santa Lúcia. Only a couple of duplicates were used for the Santo Antonio well. For the Sonja well, six pairs of duplicates were used and each pair of duplicates was collected on a

different day. For the Verônica well, three pairs of duplicates were collected, which were bottled on the same day.

For the Verônica well, three samples were collected from the following filling days: 24th, 41st, 42nd, 55th, 56th, 58th, 62nd and 64th day. A pair of duplicates from the 51st were collected. Two pairs of duplicates were collected on the 57th and 71st day.

There was no systematic sampling in relation to the quantity of packages to be collected in each season of the year. The quantity obtained for each station depended on the availability and permission for access to the eight water sources.

RESULTS AND DISCUSSION

The analysis results are shown in Table A.1 in the Appendix. The statistical summary for the analysis results is shown in Table B.1 in the Appendix. The parameters to build the temporal variograms are in Table C.1 in the Appendix.

The analysis of the statistical results in Table B.1 presented very interesting and surprising results. For the Santo Antonio, Sonja and Juliana sources, from which duplicates were collected, they show a high variation coefficient, greater than 50%. Duplicates were collected for the Verônica well, but the variation coefficient was less than 50%. It was expected that Verônica would also have a variation coefficient greater than 50%, but the result obtained was different.

No duplicates were collected for Ycuara and Primavera. These wells had a variation coefficient of less than 30%, as expected. No duplicates were collected for the Água Santa well, but this well had a much higher coefficient than the Ycuara and Primavera wells.

It can be presumed that the high coefficient of variation is also due to analytical errors made by the laboratories, and possibly the high values obtained for the coefficient of variation are not only correlated with the use of duplicates, but also with accuracy errors that are due to using the fluoride analysis method, the SPADNS method.

Table D.1 in the Appendix shows all the calculations for the extension variance. It contains the extension variance calculated for the time interval that begins in 1 day and it finishes in 2,048 days.

In Table D.1, in the seventh column, is presented the value of the percentage of the total variance of the data that corresponds to each sampling interval. Through this column and based on the data in Table D.1, it is possible to detect in which weather season of the year there was the greatest variation in fluoride data.

The sampling campaign of the Santo Antonio well started on 12/17/2015 in the spring. The highest percentage of variance occurred over the interval between 32 and 64 days, and the values reached were 43.33% and 68.33% respectively. The corresponding dates were 01/18/2016 and 02/19/2016, in the Brazilian summer.

Sampling of the Sonja well began on 12/09/2015, in the summer. Only in the Brazilian winter, after 256 days, on 08/21/2016, a percentage of 48.78% of the total variance was reached.

The Santa Lúcia well started to be sampled on 11/01/2018, during the spring. In the 64-day and 128-day intervals, the following percentages of variance were reached, respectively: 42.50% and 77.50%. These intervals respectively correspond to the dates of 01/04/2019 and 03/09/2019, in the summer weather season.

The Juliana well sampling campaign started on 08/11/2016, in the winter. Only after the 128-day interval, on December 17th, 2016, in the spring, it reached a percentage of 44.73% of the data variance.

The sampling of the Verônica well began on 06/07/2017 in the autumn. In 128 days, on 10/13/2017, in the spring season, a percentage of 82.17% of the total variance was reached.

The sampling of the Água Santa well began on 07/05/2017 in the winter. After 64 days, on the date of 09/07/2017, still in the winter season, a percentage of 72.44% was reached. After 128 days, on the date of 10/11/2017, in the spring, the percentage of variance corresponded to 102.78%.

The sampling of the Primavera well began on 08/07/2017 in the winter. Only after 256 days, on the date of 04/20/2018, in the autumn, a percentage of 54.53% of the total variance was reached.

The sampling of the Ycuara well started on 08/17/2017 in the winter. In the interval of 64 days, in the spring of 10/20/2017, a percentage of 38.88% of the total variance was reached. After 128 days, on 12/23/2017, in summer, the percentage of variance was 67.09%.

The average values obtained for the pH of the samples were: $pH = 6.7$ for the Santo Antonio well; $pH = 7.4$ for

the Sonja well; pH = 6.4 for the Santa Lúcia well; pH = 6.8 for the Juliana well; pH = 6.4 for the Verônica well; pH = 7.42 for the Primavera well; pH = 7.29 and pH = 7.27 for the Ycuara well.

Tables E.1 and E.2 show the calculations of the relative errors for confidence intervals equal to 68% and equal to 99.9% for the eight water sources.

Figures 1 and 2 show the graphs of the relative error as a function of the sampling interval for all sources; in Figure 1 the confidence interval is CI = 68% and in Figure 2, the confidence interval is 99.9%. The Juliana well is the one whose number of samples collected was not enough. The data curve for Juliana is always above the curves for the other wells. This is possible to see in the two graphs. With the sampling interval equal to 2,048 days, Juliana is the well with the greatest sampling error for the two calculated confidence intervals.

Regarding the maximum and minimum values that were calculated, a minimum negative value for fluoride was obtained for the following wells: Santo Antonio, Sonja and Juliana for the following collection intervals:

- 2,048 days for the Santo Antonio well;
- 2,048 days for the Sonja well;
- 1,024 and 2,048 days for the Juliana well.

The negative values obtained were due to analysis and measurement errors made by the chemical analysis laboratories of mineral waters.

Regarding the maximum value obtained with the sampling errors, no value was obtained that exceeded the maximum allowed value for fluoride in Brazilian legislation, which is 1.5 milligrams of fluoride per litre.

Based on the results obtained in calculating the extension variance and making a comparison with the work of Kovács *et al.* (2012), it was decided to adopt a sampling interval equal to two days for all mineral water sources.

In the work of the authors Kovács *et al.* (2012), temporal variograms were used to determine the best sampling interval for nitrate present in groundwater. The concept of extension variance was not applied in this work. The authors obtained a sampling interval equal to three days, which would guarantee the smallest sampling error for nitrate.

The sampling frequency chosen for the eight sources is two days. With this sampling interval it is possible to guarantee a relative sampling error of less than 12% for the eight sources of mineral water in the confidence intervals equal to 68% and 99.9%.

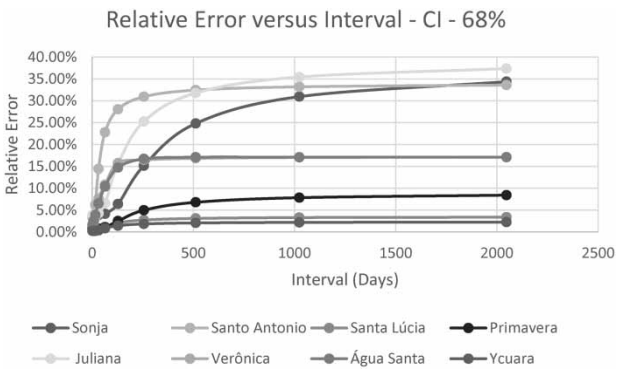

Figure 1 | Graphic of sampling interval versus relative error with CI = 68%.

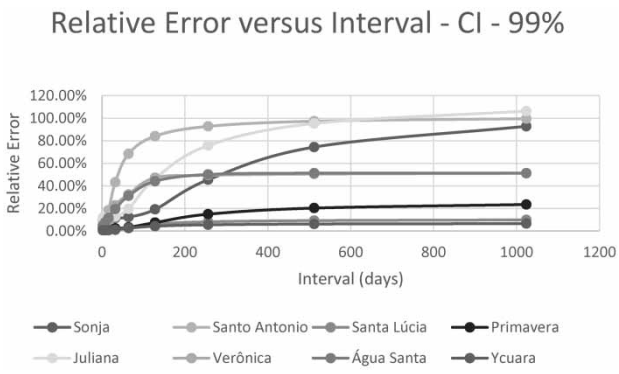

Figure 2 | Graphic of sampling interval versus relative error with CI = 99.9%.

CONCLUSIONS

For fluoride sampling, it was concluded that the best sampling frequency is to collect samples every two days. This collection interval is somewhat feasible if implemented in a mineral water industry and will allow the obtaining of an appropriated number of samples to be analyzed as a Gaussian distribution in the future.

The new sampling campaign should collect more duplicates, that is, for all sampled wells, samples that were filled on the same day and at different times, as well as samples that were filled on the same day and at the same time, should also be collected. Samples filled at different times and days will be collected. The use of replicates is also foreseen, because in the present work, replicates of the packaging were not used.

It will be essential to collect blank samples, and in the case of mineral water, samples of deionized water will be analyzed to test whether the laboratories are carrying out the chemical analyses correctly.

The sampling errors that were found were due to the analytical errors made by all the laboratories that carried out the analysis of the eight sources studied. A priori, there was no collection error because the packages were purchased in commercial establishments and taken to the analysis laboratory.

The packages were not opened and there was no fractioning of the contents, to ensure that the collection process and the sample preparation process did not generate sampling errors and interfere with the analysis results.

No blank samples were used in the first moment for this work because it was necessary to quantify in percentages how much the errors in the analyses are interfering in the relative error in order to define the correct percentage of blank samples to be adopted in the new sampling campaigns.

Based on the above, new sampling campaigns for the sources that constituted the object of this work will be initiated, as soon as financial resources are obtained so that the fluoride analyses can be carried out in the same period of time for all sources.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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